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Development of Polymer from High Internal Phase Emulsion for CO_2 Adsorption

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Abstract

Polyvinylbenzyl chloride-divinylbenzene was prepared using the high internal phase emulsion (HIPE) technique and modified with ethylenediamine and triethylenetetramine. All adsorbents were characterized witha fourier transform infrared spectrometer, elemental analyzer, and surface area analyzer. These adsorbents were to be used as adsorbents for a CO_2 adsorption study. The experiments were carried out at room temperature and atmospheric pressure using dry 4% CO_2/N_2 feed gas. The adsorption capacity results showed that the triethylenetetramine adsorbent (0.3283 mmolCO_2/g-adsorbent) had a greater adsorption capacity than the ethylenediamine adsorbent (0.3172 mmol CO_2/g-adsorbent).

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Keywords: CO_2 adsorption; high intenal phase emulsion; adsorbent; carbon dioxide; amine functionalization.

1. Introduction

The top three greenhouse gases (GHG) are; CO_2 (72%), CH_4 (18%), and N_2O (9%). CO_2 is considered the most important GHG because it is released in the largest quantities. Various techniques have been developed to minimize the emission of GHG such as cryogenic capture, membrane technology, absorption technology, adsorption technology, as well as microbial/ algal system [1-7]. A typical technology which is

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widely used to separate CO_2 in gas processing is absorption using an aqueous alkanolamine based on reversible chemical absorption of CO_2 via an acid-base reaction. However, it causes some serious problems such as oxidative degradation of the alkanolamine solution, it also causes corrosionand foaming in the gas-liquid interface, and there is a large energy requirement for regeneration [5, 8-10]. Adsorption is one technique that is widely used to as an alternative. There are various kinds of adsorbents used in this technique, for example, activated carbon, zeolite, SBA-15 mesoporous silica, carbon nanotubes, and mesoporous molecular sieve MCM-41[11-14]. In addition, the capability of these adsorbents can be improved by introducing amine functional groups into the adsorbents via grafting or impregating with diverse amine species. Amine groups are dispersed inside the pore of the adsorbent and enhance CO_2 capture performance.There are various amine types have been used to modify adsorbents such as 3-aminopropyltriethoxysilane, N-(2-aminoethyl)-(3-aminopropyl)triethoxysilane, 3-aminopropyl-trimethoxysilane, diethylenetriamine, tetraethylenepentamine, pentaethylenehexamine, and polyethyleneimine [11, 15-18].

In this work, we were interested in materials that were prepared by the high internal phase emulsion (HIPE) technique, called polyHIPEs. This material was modified with amines and used as an adsorbent for this study.

Nomenclature

C_{in}	Concentration of CO_2 entering the reactor, vol%
C_{out}	Concentration of CO_2 downstream the reactor, vol%
F	Total flow rate, mol/min
M	weight of adsorbent, g
Q_{ads}	Dynamic adsorption capacity, molCO_2/mol amine
t_{st}	Stoichiometric time corresponding to CO_2 stoichiometric adsorption capacity, min
t	Time at which the C_{out} reaches its maximum permissible level, min.

2. Experiment

2.1 Poly (VBC-co-DVB) preparation

Porous adsorbents were prepared as emulsions. These emulsions were prepared by slowly adding an aqueous phase containing water, initiator, and stabilizer into an oil phase containing a vinylbenzylchloride (VBC) mononer and a divinylbenzene (DVB) co-monomer, poragen, and a surfactant under constant agitation for 1h to produce a water-in-oil emulsion.Then it was poured into a cylindrical mold and further polymerized at 70 °C for 24 h. The adsorbents were removed from the mold and extracted with hot ethanol in a soxhlet extractor for 6 h and dried to a constant weight in a vacuum oven at 60 °C for 48 h.

2.2 Amine functionalization of poly (VBC-co-DVB)

The procedure for amine functionalization was adopted from the Stefance and Krajnc method [23]. Two alkanolamines, (ethylenediamine and triethylenetetramine) were used. Poly(VBC-co-DVB) was cut into 2 cm (length) × 2 cm (diameter) pieces and immersed in the amine solution which was prepared by mixing amine (2.629 mmol) in 10 mL of N, N-dimethylformamide (DMF). The resulting mixture was left at room temperature for 1 h and then put into a water bath (80 °C) for 24 h. After the reaction completed, the sample was filtered and washed with DMF, EtOH, EtOH/ H_2O (1:1 v/v), EtOH/ THF (1:1 v/v), and THF, respectively, left at room temperature for 30 min and dried in a vacuum oven at 60 °C for 24 h.

2.3 Characterization

All adsorbents were characterized, to observe the surface morphology, using a scanning electron microscope (SEM). Prior to analysis, samples were dried in the oven at 80 °C overnight, and then cut cross-sectionally. Samples were put on an aluminium stub with conductive carbon tape and coated with platinum. Specific surface area was investigated by a N_2 adsorption measurement using a surface area analyzer. The sample was dried at 100 °C in the vacuum oven before analysis. The IR spectra of all adsorbents were recorded using a Fourier transform infrared (FTIR) spectrometer, while using the KBr pellet technique to determine amine functionalization. Additionally, the conversion rate of amine functionalization was determined by the nitrogen content loaded in the adsorbents using an elemental analyzer and chloride titration method.

2.4 CO_2 adsorption study

The capability of the adsorbents was expressed in terms of dynamic adsorption capacity (Q_{ads}) which can be calculated by eq. 1 and eq. 2 [20],

$$Q_{ads} = \frac{FC_{in}t_{st}}{M} \quad (1)$$

$$t_{st} = \int_0^t \left(1 - \frac{C_{out}}{C_{in}}\right) dt \quad (2)$$

The experimental setup for CO_2 adsorption is shown in Fig. 1. A piece of solid amine-based adsorbent was loaded into the reactor and pretreated in N_2 gas flow (20 mL/min) at 60 °C for 1 h before allowing CO_2 to enter the reactor. At room temperature, the N_2 flow was then switched to 4 vol% of CO_2 in N_2 balance at a total flow rate of 5 mL/min. The concentration of CO_2 was measured by gas chromatography (GC) and the adsorption breakthrough points were determined after the adsorption process reached equilibrium.

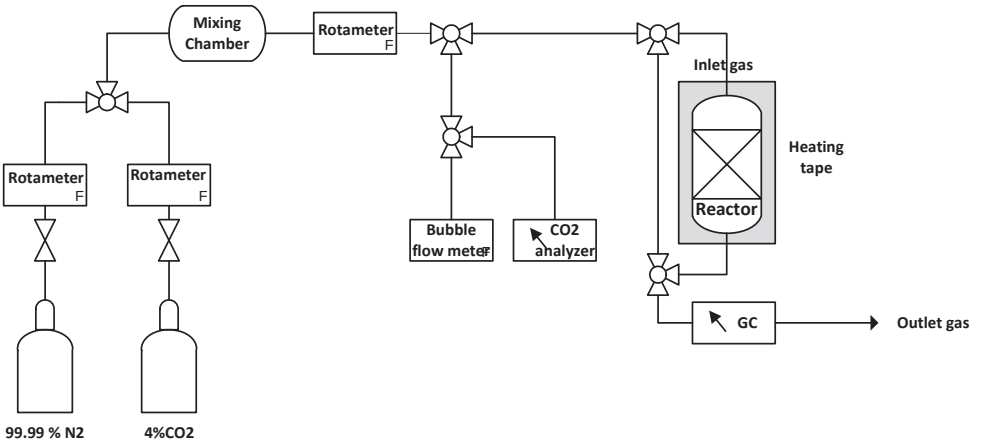

Fig.. 1. Experimental setup for CO_2 adsorption study

3. Results and Discussion

3.1 Preparation of alkylamine-based adsorbents

Adsorbent templates are polymer materials prepared by the high internal phase emulsion technique, called polyHIPE. In this work polyHIPE was synthesized using VBC and DVB as monomers. The poly(VBC-co-DVB)HIPEs were modified with the alkanolamines—ethylenediamine and triethylenetetramine. Amine functionalization in poly(VBC-co-DVB) occurred via nucleophilic substitution reaction at the methylene chloride group (-CH_2-Cl). This reaction was determined using FTIR where the disappearance of C-Cl wagging and stretching vibrations at 1265 cm^{-1} and 710 cm^{-1} and the presence of N-H stretching and bending vibrations at 3400 cm^{-1} and 1670 cm^{-1} were observed as shown in Fig. 2. The conversion rate of amine functionalization of all adsorbents is shown in Table 1 which was calculated by using the elemental analysis data of nitrogen content and chloride content as shown in Eq. 3 and Eq. 4.

$$\text{ConversionA}(\%) = \frac{(\text{Chloride}_{\text{origin}} - \text{Chloride}_{\text{remaining}})}{\text{Chloride}_{\text{origin}}} \times 100 \quad (3)$$

$$\text{ConversionB}(\%) = \frac{\text{Nitrogen}_{\text{found}}}{\text{Nitrogen}_{\text{calculated}}} \times 100 \quad (4)$$

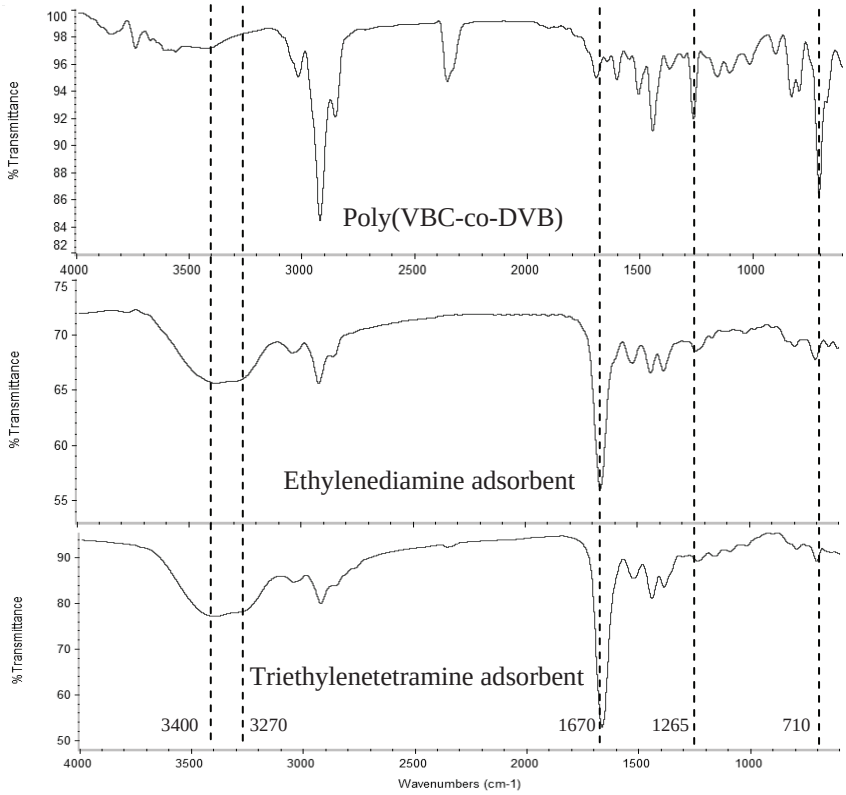

Fig.. 2. FTIR spectra of amine functionalized poly(VBC-co-DVB) adsorbents

Table 1 Elemental Analysis data and conversion of amine functionalization

Adsorbent	Chloride[a] (A)		Nitrogen[b] (B)		Conversion(%)	
	%	mmol/g	%	mmol/g	A	B
65 %DVB polyHIPE	7.99	2.250				
Ethylenediamine	0.30	0.084	6.43	4.59	96.25	95.97
Triethylenetetramine	1.30	0.365	9.69	6.92	83.78	87.22

[a] by Cl titration

[b] by CHN elemental analyzer

A based on the remaining chloride

B calculated from the percentage of Nitrogen in the product

Conversion A was calculated based on the remaining chloride in the adsorbent. Conversion B was calculated from the amount of nitrogen in the adsorbent. It was found that the conversion of the reaction between poly(VBC-co-DVB) and the amine was affected by the structure of amine use. If the amine structure is quite bulky or has a branch chain, the conversion rate will be lower. Ethylenediamine showed a higher conversion rate (96.25 % conversion A and 95.97 % conversion B due to its small structure, is quite which lead to an easily reacts with the methylene chloride group in poly(VBC-co-DVB). On the contrary, triethylenetetramine is bulkiere which it made rather difficult to functionalize.

In addition, the surface properties of polyHIPEs were also affected after amine functionalization (Table 2). The unmodified polyHIPE had 151.77 m^2/g of surface area, 0.3135 cm^3/g of total pore volume and 169 nm of average pore size. Pore size of the modified polyHIPE decreased when compared with the unmodified one due to the blockage of pores by the amine functional group at the external and internal surface of the polyHIPE which resulted in decreasing pore size and led to decreasing surface area and pore volume of the polyHIPE.

Table 2 Porosity properties, amine content, and adsorption capacity of adsorbents

Adsorbents	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
Unmodified adsorbent	151.77	0.3135	169.1066
Ethylenediamine	50.785	0.1116	123.7505
Triethylenetetramine	74.465	0.1549	138.4789

3.2 CO_2 adsorption study

The adsorbents were first pretreated by heating to 100 °C then cooled to room temperature in a N_2 flow to remove remaining moisture before performing adsorption. The adsorption study was carried out at room temperature with 4% CO_2/N_2 at a flow rate of 5 ml/min. The adsorption data were recorded continuously by GC and presented as a breakthrough profile (Fig. 3).

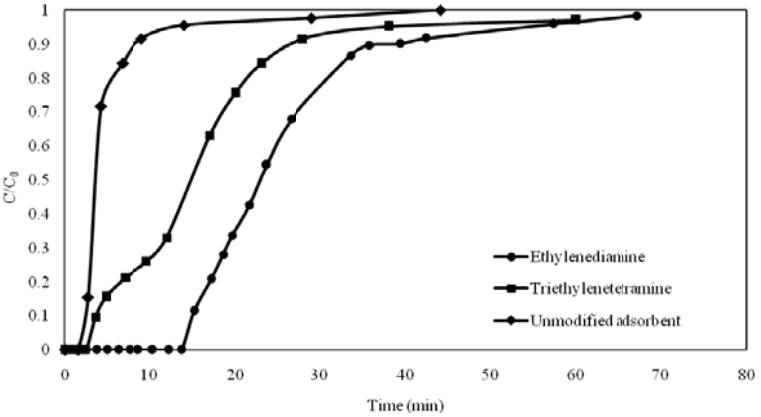

Fig. 3. Breakthrough curve profiles of adsorbents

The adsorption capacities of the ethylenediamine- and triethylenetetramine-based adsorbents were 0.3171 mmolCO_2/g and 0.3283 mmolCO_2/g, respectively, which were higher than that of the unmodified adsorbent (0.1063 mmolCO_2/g) due to the enhancement of the interaction of CO_2 with amine on the surface of the adsorbent [12]. The adsorption capacity of triethylenetetramine based adsorbent was higher than that of the ethylenediamine based adsorbent. The nitrogen content in the triethylenetetramine-based adsorbent was higher than that of the ethylenediamine-based adsorbent, which led to a higher adsorption capacity.

4. Conclusion

Poly(VBC-co-DVB) was modified with ethylenediamine and triethylenetetramine by post-functionalization to enhance CO_2 adsorption capacity. The surface properties and adsorption capacity indicate that the fundamental pore structure of the adsorbents decrease after modification. The triethylenetetramine-based adsorbent showed the highest dynamic adsorption capacity. For further work, amine compounds which have higher amount of nitrogen should be used to improve the adsorption capacity of adsorbent.

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References

[1] Douglas A, Costas T. Separation of CO_2 from flue gas: A review. *Separation Science and Technology* 2005;**40**(1-3):321-348.

[2] Kikkinides ES, Yang RT, Cho SH. Concentration and recovery of CO_2 from flue gas by pressure swing adsorption. *Industrial and Engineering Chemistry Research* 1993;**32**:2714-2720.

[3] Hyun SH, Song JK, Kwak BI, Kim JH, Hong SA. Synthesis of ZSM-5 zeolite composite membranes for CO_2 separation. *Material Science* 1999;**34**:3095-3103.

[4] Peter JEH, Abdelhamid S. Applications of pore-expanded mesoporous silica.5.Triamine grafted material with exceptional CO_2 dynamic and equilibrium adsorption performance. *Industrial and Engineering Chemistry Research* 2007;**46**:446-458.

[5] Robert JH, An investigation of some sterically hindered amines as potential carbon dioxide scrubbing compounds. *Industrial and Engineering Chemistry Research* 1997;**36**:1779-1790.

[6] Tan CS, Chen JE. Absorption of carbon dioxide with piperazine and its mixtures in a rotating packed bed. *Separation and Purification Technology* 2006;**49**(2):174-180.

[7] Gupta M, Coyle I, Thambimuthu K. In *Strawman document for CO_2 Capture and Storage(CC&S) technology roadmap*. Canada; 2003.

[8] Chakma A. CO_2 capture processes-opportunities for improved energy efficiencies. *Energy conversion and management* 1997;**38**:S51-S58.

[9] Veawab A, Tontiwachwuthikul P, Chakma A. Corrosion behavior of carbon steel in the CO_2 absorption process using aqueous amine solutions. *Industrial and Engineering Chemistry Research* 1999;**38**(10):3917-3924.

[10] Bello A, Idem RO. Comprehensive study of the kinetics of the oxidative degradation of CO_2 loaded and concentrated aqueous monoethanolamine (MEA) with and without sodium metavanadate during CO_2 absorption from flue gases. *Industrial and Engineering Chemistry Research* 2006;**45**(8):2569-2579.

[11] Zhijuan Z, Mingyao X, Haihui W, Zhong L. Enhancement of CO_2 adsorption on high surface area activated carbon modified by N_2, H_2 and ammonia. *Chemical Engineering Journal* 2010;**160**:571-577.

[12] Ravikrishna C, Amit AK, Ransiwal JA, Thote VK, Pravin J, Satish KL, Rajesh BB, Nitin KL, Sadhana SR. Amine loaded zeolites for carbon dioxide capture: Amine loading and adsorption studies. *Microporous and Mesoporous Material* 2009;**121**:84-89.

[13] Chang FY, Chao KJ, Cheng HH, Tan CS. Adsorption of CO_2 onto amine-grafted mesoporous silicas. *Separation and Purification Technology* 2009;**70**:87-95.

[14] Hsu SC, Chungsying L, Fengsheng S, Wanting Z, Wenfa C. Thermodynamics and regeneration studies of CO_2 adsorption on multiwalled carbon nanotubes. *Chemical Engineering Science* 2010;**65**:1354-1361.

[15] Zelenal V, Halamova D, Gaberova L, Bloch E, Llewellyn P. Amine-modified SBA-12 mesoporous silica for carbon dioxide capture: Effect of amine basicity on sorption properties. *Microporous and Mesoporous Material* 2008;**116**:358-364.

[16] Gerhard DP, Stefanec CG, Sylvania L, Alexandra C, Bruno D. Amines immobilized on a solid support for postcombustion CO_2 capture-A preliminary analysis of the performance in a VSA or TSA process based on the adsorption isotherms and kinetic data. *Energy Procedia* 2009;**1**:1335-1342.

[17] Plaza MG, Pevida C, Arenillas A, Rubrier F, Pis JJ. CO_2 capture by adsorption with nitrogen enriched carbons. *Fuel* 2007;**86**:2204-2212.

[18] Shiyou H, Qiang X, Hui Y, Yijun Z, Francesco P, Weidong Z. Synthesis and CO_2 adsorption property of amine-functionalized silica nanospheres with centrosymmetric radial mesopores. *Microporous and Mesoporous Material* 2010;**132**:552-558.

[19] Stefanec D, Krajnc P. 4-vinylbenzyl chloride based porous spherical polymer supports derived from water-in-oil-in-water emulsions. *Creative & Functional Polymers* 2005;**65**:37-45.

[20] Geankoplis CJ. *Transport Processes and Unit Operations*. 3rd ed. New Jersey:Prentice-Hall;1993.

[21] Filburn T, Helble JJ, Weiss RA. Development of supported ethanolamines and modified ethanolamines for CO_2 capture. *Industrial and Engineering Chemistry Research* 2005;**44**(5):1542-1546.